Magnetic-field Processing as a Means of Extending Structural Ordering in Self-assembled Biomimetic Gels

Post-self-assembly processing of hierarchically-organized complex systems to produce materials with enhanced structural ordering and, hence, improved physical properties, is an area of considerable current interest. Here, we report the use of small-angle diffraction at the Advanced Photon Source as a means of probing the magnetic field-induced alignment in a biomembrane-mimetic gel. This work demonstrates that post-self-assembly processing can be used to convert poorly organized materials, such as complex fluids, into materials of well-defined structure.

A major area of current research interest in the field of materials science is the development of hierarchically organized complex systems to produce materials with novel structure or properties. One approach involves the use of self-assembly. The harnessing of self-assembly to produce functional aggregates poses a significant challenge, since frequently it leads to disordered (polymicrodomain) structures, limiting the utility of these materials. Potential areas of application include the development of biomimetic materials capable of organizing membrane proteins for structure and function studies in native-like environments or harnessing their evolutionarily optimized functions as the basis of devices applicable in the areas of catalysis or photonics [1-4]. Although much effort has been directed at the study of the design principles of self-organizing molecular assemblies, considerably less attention has focused on the use of post-assembly processing as a means of converting poorly organized materials, such as complex fluids, into useful/functional materials of well-defined structure [5]. Here, we examine the magnetic-field-induced alignment of a recently developed biomembrane-mimetic gel using synchrotron small-angle x-ray diffraction [6-8].

Ex situ magnetic-field studies were carried out on samples in 1.5 mm quartz capillaries that were then inserted into a 5 mm nuclear magnetic resonance (NMR) tube. Magnetic-field alignment of the sample was achieved in the superconducting magnet (7.05 T) of a GE Omega 300 NMR spectrometer. The sample temperature was controlled via dry-ice-cooled N_2 gas flow. In the presence of the field, the sample was cooled to 2ºC and held for 1 h, then gradually (over a 30 min period) warmed to 25ºC, held an additional 1 h, and then removed from the magnet. Aligned samples were stored at room temperature until taken for x-ray studies. Synchrotron small-angle x-ray diffraction measurements were performed at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) undulator beamline (12-ID) of the Advanced Photon Source at Argonne National Laboratory. The scattering profiles were recorded with a mosaic detector composed of 9 CCD chips with an imaging area of 15 × 15 cm, with 1536 × 1536 pixel resolution. The area detector images were corrected for background scattering of water by subtracting from the recorded images an area detector image of a water sample obtained with the same total exposure time as for the liquid crystalline sample (5 s). The collected low-angle scattering data were calibrated based upon the known positions of silver behenate powder Bragg reflections.

In this work [8], we describe the magnetic-field-induced alignment of a recently developed polymer-grafted lipid-based complex fluid [6,7] consisting of a four-component mixture of water, a phospholipid, a lipopolymer comprising poly(ethylene) oxide terminally grafted onto a phospholipid headgroup, and a co-surfactant. Interestingly, this material is found to exhibit an inverted, thermo-reversible phase transition from a nonbirefringent, low-viscosity state to a liquid-crystalline (birefringent), elastic solid or gel as the sample is warmed above 16ºC. In previous reports, Firestone and co-workers described the structural characterization of this complex fluid employing a variety of spectroscopic and scattering techniques [6,7]. These studies revealed that, at room temperature, the molecular components of this system self-assemble to form ordered microdomains of lamellae, while below the phase transition (16ºC), the material exists as a 2D hexagonal array of micellar cylinders. Our subsequent work has demonstrated that membrane- and aqueous-soluble proteins and metal or semiconductor nanoparticles can be readily introduced into the cold phase of this material, transferred into the ordered lamellar phase (liquid crystalline state), and organized in the hydrophobic (alkane) or water domains by simply warming the sample to above the phase transition temperature [9,10]. In this work, we demonstrate the use of an applied magnetic field as a means of aligning the lamellar (sheet-like) microdomains, thereby eliminating unfavorable orientation and defects in this material and extending the order into macroscopic dimensions.

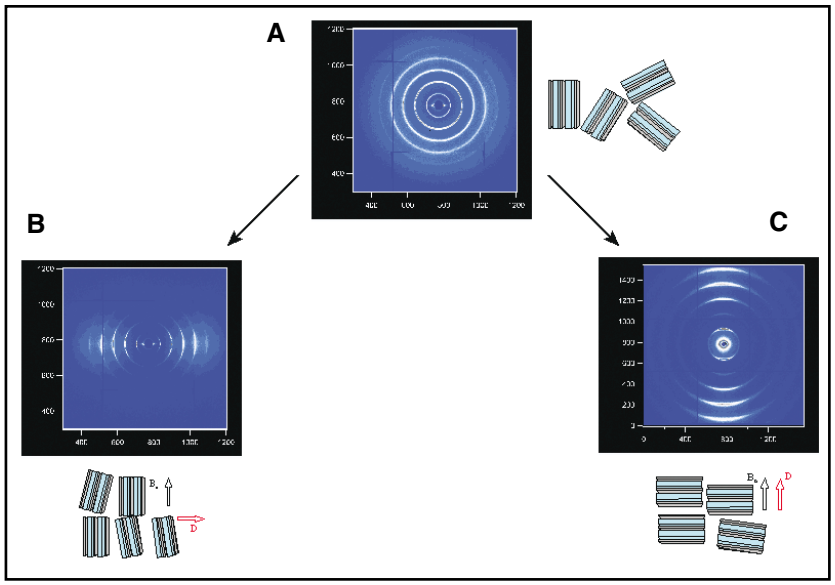

FIG. 1. Effects of magnetic field processing on the structure of the complex fluid as measured by small angle x-ray diffraction. (A) Isotropic Bragg rings observed in the 2D x-ray pattern prior to magnetic field processing indicating a mosaic (random) distribution of sheet-like lamella. (B) Anisotropic diffraction pattern observed in the 2D SAXS pattern after magnetic field processing indicating preferential alignment of the lamellar domains perpendicular to the applied field axis. (C) Anisotropic diffraction pattern produced after magnetic field processing with incoporation of paramagnetic Lanthanide reagents.

Persistent structural changes/enhanced asymmetry can be induced in the gel phase of the complex fluid by modest exposure to a magnetic field [8]. This effect is observed by comparing the 2D small-angle x-ray scattering (SAXS) patterns of the unaligned and aligned gels (Figs. 1a and b, respectively). The isotropic 2-D intensity pattern observed for the gel phase prior to magnetic-field processing (Fig. 1a) indicates that it is a mosaic structure consisting of lamellar microdomains in which all spatial orientations are present. After magnetic-field alignment below the phase transition temperature followed by warming in the presence of the field, a strong anisotropic 2-D scattering pattern is observed (Fig.1b), indicating long-range ordering of the lamellar domains. The anisotropy about the equatorial axis indicates that the lamellae preferentially orient perpendicular to the magnetic field direction. This field-induced anisotropy extends to macroscopic dimensions and persists even after removal from the field, as evidenced by the dramatic changes observed in the optical birefringence pattern (Fig. 2). The high degree of persistent anisotropy is achievable due to the inverted, thermoreversible phase transition characteristic of the complex fluid. That is, macroscopic alignment is achieved by the nucleation of highly aligned cylinderical micelles (in the presence of the

magnetic field) from the low-viscosity micellar phase into extended liquid-crystalline domains of the lamellar gel phase.

The ability to design and produce anisotropic media that can be oriented both perpendicular and parallel to the applied field direction is important for the development of materials useful for both structure-function studies of biomolecules and to the development of nanostructured composite materials for device applications. To this end, we have examined the effect of the addition of paramagnetic (lanthanide ions) to the composition prior to magnetic-field exposure. The effect was monitored by comparing the 2D SAXS patterns of an unaligned, lanthanide-doped sample to one that had been subjected to moderate magnetic-field exposure (Fig. 1c). The results indicate that the alignment of the lamellar domains can be switched/flipped 90º (lamellae oriented parallel to the applied field direction) by introduction of these agents.

This work demonstrates that post-self-assembly processing can be used to convert poorly organized materials, such as complex fluids, into materials of well-defined structure. These results, in conjunction with other known features of the complex fluid (e.g., excellent optical transparency and the ability to encapsulate a wide range of molecules, including membrane proteins) suggests that this material offers enormous potential as platform for the development of functional self-assembled materials and for conducting fundamental physicochemical studies of proteins that have eluded crystallization of biomolecules in their native-like environments.

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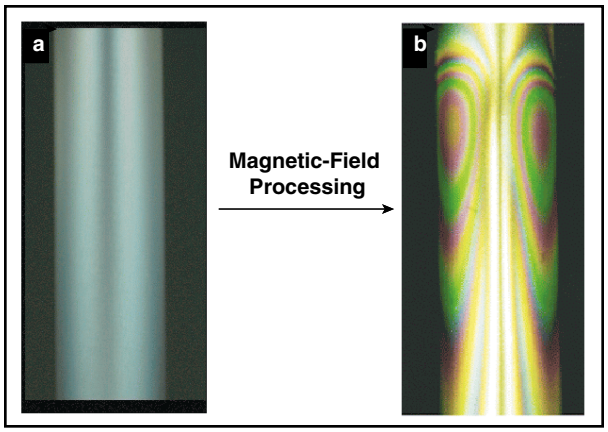

FIG. 2. Polarized optical micrograph of the complex fluid in the gel phase viewed between crossed polarizers (a) at 23ºC prior to magnetic field processing and (b) after magnetic field processing at 7 T.

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